Review Notes on Point Groups and Symmetry
from undergraduate Inorganic Chemistry I course

I. Introduction

The major difference between organic and inorganic molecules is that organic molecules contain carbon and hydrogen atoms. Inorganic molecules are all compounds that do not contain carbon and hydrogen.

Some points regarding inorganic molecules:

- They often contain transition metals
- Valence electrons in d-orbitals in transition metals are involved in bonding
- s, p, d orbitals can be used in bonding (hybridization)
- More bonds and geometries are possible around the central atom compared to bonds around a carbon atom

Greater geometric complexity in inorganic molecules (about the central atom)

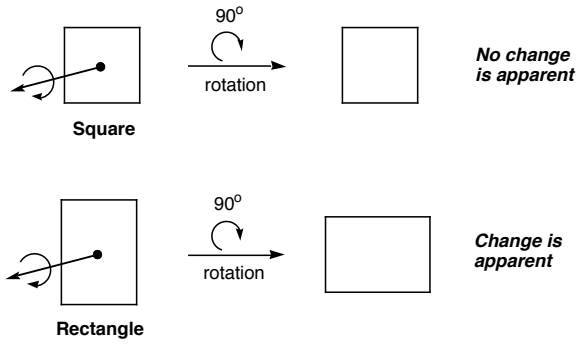
GEOMETRY <— *related* —> SYMMETRY

Symmetry plays a role in the physical properties of molecules, such as

- *Bonding*- which orbitals interact to form bonds
- *Absorption spectra*
  - Energy of transitions (position)
  - Transitions allowed or forbidden (intensity)
- *Magnetic properties*- number of unpaired electrons
- *Packing* of molecules in crystal lattice determines solid state structure and properties

II. Symmetry of Objects and Molecules

Compare a square to a rectangle. Which is more symmetrical? Why?



A 90° rotation from the center about an axis perpendicular to the paper leaves cube unchanged, but not the rectangular object. In general, the square has more rotations & reflections that leave it unchanged, there are not as many for the rectangle. This makes the square more symmetrical than then rectangle.

We need to relate these symmetry attributes to molecules.

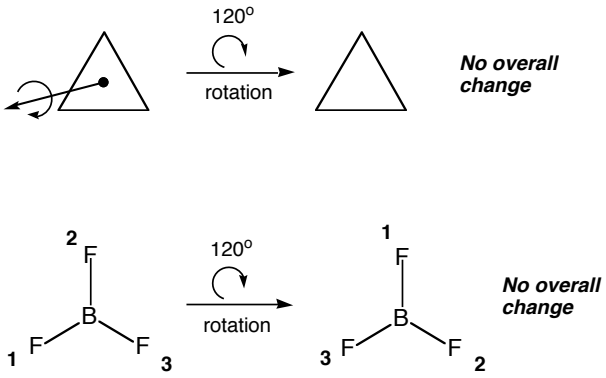
In general, we define

Symmetry: invariance to transformation

Transformation: movement of molecule (rotation, reflection, etc.)

For example, compare the rotation of an equilateral triangle by 120° with that of a trigonal planar molecule, BF_3. When the triangle is rotated, no overall change is apparent. Although the F's were interchanged in BF_3, we cannot tell because all F's are equivalent, therefore, if we had not numbered the F atoms, we would say that the molecule was left unchanged.

Therefore, for BF_3, a 120° rotation ⊥ to the plane of the molecule leaves the molecule unchanged. We say that this transformation is a symmetry operation of the BF_3 molecule.



Symmetry operation: a movement of a molecule that leaves the object or molecule unchanged

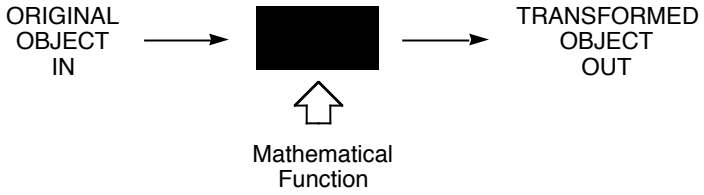
Symmetry element: feature of the molecule that permits a transformation (operation) to be executed which leaves the object or molecule unchanged.

Each symmetry operation has a symmetry element associated with it. The ones will be concerned with here are listed below.

Operation	Element
Rotation	Axis of rotation
Reflection	Mirror plane
Inversion	Center of inversion
Improper rotation	Axis of improper rotation

The symmetry of a given molecule depends which type and how many operations leave it unchanged. Before we go over the symmetry of molecules we will discuss all the operations and their mathematical forms (handout on symmetry operations, matrices).

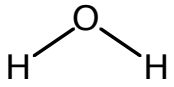
In general, an operation can be thought of as a black box that moves or does something to an object



A. Symmetry Elements and Operations

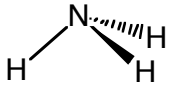
1. Mirror Plane, Reflection operation (σ)

How many mirror planes are there in H_2O? Total: 2 σ



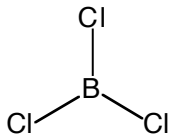
- 1 σ bisecting the H-O-H bond (⊥ to paper)
- 1 σ in the plane of the molecule (contains plane of paper)

How about NH_3? Total: 3 σ



- 1 σ contains each N-H bond and bisects H-N-H

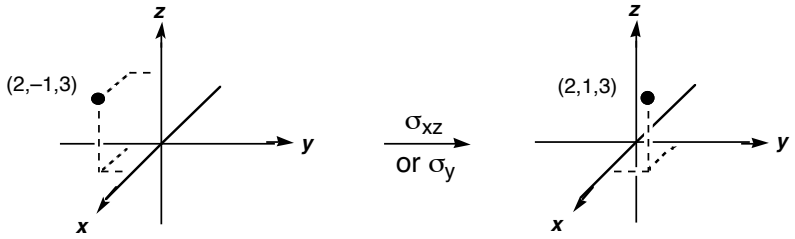
BCl_3 (planar molecule)? Total: 4 σ



- 3 σ ⊥ to plane of the molecule along each B-Cl bond
- 1 σ in the plane of the molecule (contains all atoms)

Planar $[PtCl_4]^{2-}$? Total 5 σ; similar to BCl_3

We can describe reflections are mathematically, since they are mathematical operations. For example, using Cartesian coordinates, one can ask where does a point (a,b,c) end up after reflection through xz-plane?



such that

$$(2,-1,3) \xrightarrow[\text{or } \sigma_y]{\sigma_{xz}} (2,1,3)$$

or, in general,

$$(a,b,c) \xrightarrow[\text{or } \sigma_y]{\sigma_{xz}} (a,-b,c)$$

Similarly,

$$(a,b,c) \xrightarrow[\text{or } \sigma_x]{\sigma_{yz}} (-a,b,c)$$

$$(a,b,c) \xrightarrow[\text{or } \sigma_z]{\sigma_{xy}} (a,b,-c)$$

Each operation can be written in the form of a matrix. A 3x3 matrix is required for the transformation of an x,y,z point (a,b,c). For example, using the example above for a reflection through the xz plane, σ_{xz}, from point P at (a,b,c) to point P´ at (a,-b,c), we can write:

$$P' = \sigma_{xz}(P),$$

which means that the reflection operation on point P, σ_{xz} (P), results in P´. Since P = (a, b, c) and P´ = (a´, b´, c´) = (a, -b, c), we can write

$$(a',b',c') = \sigma_{xz}(a,b,c) = (a,-b,c)$$

Using matrices we can then write:

$$\begin{bmatrix} a' \\ b' \\ c' \end{bmatrix} = \underbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{\sigma_{xz}} \begin{bmatrix} a \\ b \\ c \end{bmatrix} = \begin{bmatrix} a \\ -b \\ c \end{bmatrix}$$

$$\mathbf{P'} \qquad\qquad \mathbf{P} \qquad \mathbf{P'}$$

Similarly, we can write the transformation matrices for σ_{yz} and σ_{xy} as follows.

$$\sigma_x = \sigma_{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \sigma_z = \sigma_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

2. Inversion, center of inversion (i)

Inversion operation: takes a point on a line through the origin to an equal distance on the other side

For a point at x,y,z coordinates (2,-3,-4) inversion would move the point to (-2,3,4), such that

$$i\,(2,-3,-4) = (-2,3,4)$$

Therefore, in general, inversion of a point (a,b,c) results in a point at (-a,-b,-c) or

$$i\,(a,b,c) = (-a,-b,-c)$$

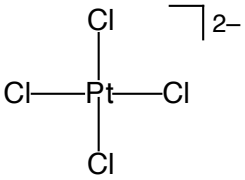
The transformation matrix for inversion is given by

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

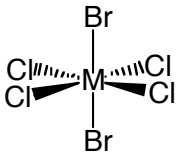
If inversion operation is a symmetry operation of the molecule then we can say that:

- the molecule possesses a center of symmetry
- the molecule in centrosymmetric

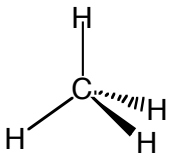
Do the following molecules have centers of inversion?



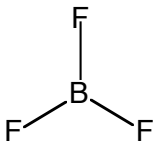
Yes



Yes



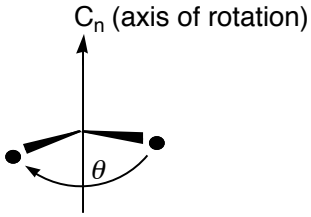
No



No

3. Rotation, Axis of Rotation (C_n)

C_n = rotation about an axis of n-fold symmetry



An object has <u>axial symmetry</u> if it is invariant to rotation by θ, where n ($n = 2\pi/\theta$) is an integer.

n is the <u>order</u> of rotation

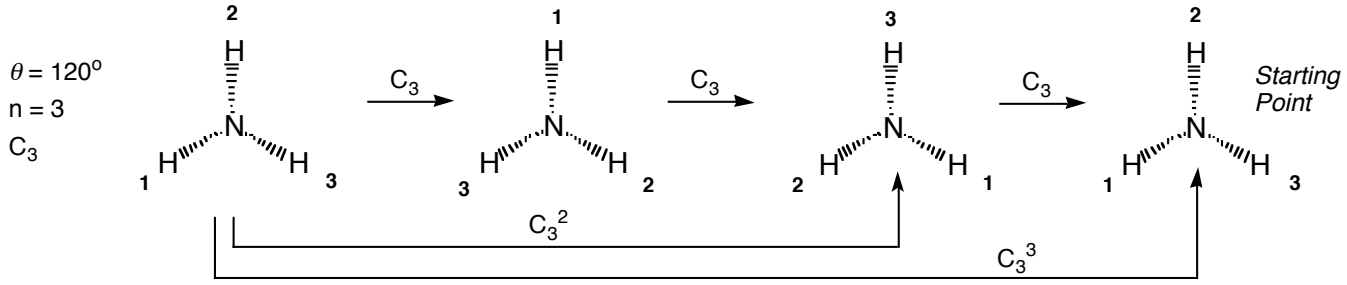
θ is the <u>angle</u> of rotation

Convention: clockwise rotation looking down axis

C_n^m means doing the C_n operation m times.

C_n^n takes the molecule back to starting position

Rotations in NH_3 (top view):



The general transformation matrix for a C_n rotation about the z-axis is given by

$$C_n^z = \begin{bmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

So for C_2 and C_4 rotations about the z-axis

$$C_2 = \begin{bmatrix} \cos(\pi) & \sin(\pi) & 0 \\ -\sin(\pi) & \cos(\pi) & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

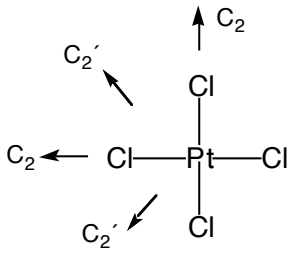
$$C_4 = \begin{bmatrix} \cos(\pi/2) & \sin(\pi/2) & 0 \\ -\sin(\pi/2) & \cos(\pi/2) & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The general matrices for C_n rotations about the x and y axes are given by:

$$C_n^x = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(2\pi/n) & \sin(2\pi/n) \\ 0 & -\sin(2\pi/n) & \cos(2\pi/n) \end{bmatrix} \qquad C_n^y = \begin{bmatrix} \cos(2\pi/n) & 0 & \sin(2\pi/n) \\ 0 & 1 & 0 \\ -\sin(2\pi/n) & 0 & \cos(2\pi/n) \end{bmatrix}$$

All linear molecules have a C_∞ axis along the axis of the molecule. They can be rotated by an infinitesimal angle and remain unchanged.

Example: List the rotational axes and operations present in square planar $[PtCl_4]^{2-}$.



Axes	Operations
$C_4 \perp$ plane of molecule	C_4, $C_4^2 = C2$, C_4^3
2 C_2 contain Pt-Cl bonds	2 C_2
2 C_2' bisect Cl-Pt-Cl	2 C_2'

4. Identity Operation: E

Identity operation leaves a molecule unchanged.

The operation E performed on a Cartesian point (a,b,c) results in (a,b,c). The matix for E is given by:

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Various operations performed successively result in placing the molecule in the original position, such as one reflection followed by another, inversion followed by inversion, and a C_n rotation performed n times, such that

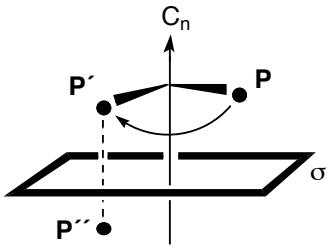
$$\sigma \bullet \sigma = E$$

$$i \bullet i = E$$

$$C_n^{\,n} = E$$

5. Improper Rotation: S_n (element= axis of improper rotation)

The improper rotation, S_n, is defined as a rotation (C_n) followed by reflection (σ) through plane perpendicular to the C_n axis.



P → P´ by C_n,
P´ → P´´ by σ

Overall, $S_n(P) = P''$

$S_n = C_n \times \sigma = \sigma \times C_n \Rightarrow$ the operations commute

We can multiply the corresponding matrices for rotation (along z-axis) and reflection to arrive at the transformation matrix for the S_n operation.

$$S_n = \sigma_{xy} \times C_n = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix} =$$

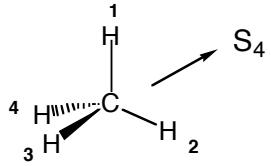
$$= \begin{bmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Doing the S_n operation m times:

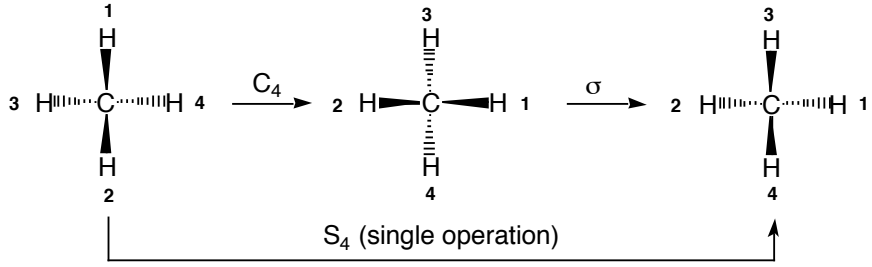
$$S_n^m = C_n^m \times \sigma^m = \begin{cases} = C_n^m \text{ if m = even} \\ = C_n^m \times \sigma \text{ if m = odd} \end{cases}$$

$$S_n^n = C_n^n \times \sigma = \begin{cases} = E \text{ if m = even} \\ = \sigma \text{ if m = odd} \end{cases}$$

Example: S_4 rotation and its repetitions on CH_4



Looking down the S_4 axis (rotating the CH_4 molecule so that S_4 arrow points at you):



Notice that there is a C_2 axis coincident with the S_4 axis that arises from doing the S_4 operation two times. The S_4 axis gives rise to the following operations:

$$S_4,\ \ S_4^{\,2} \equiv C_2,\ \ S_4^{\,3},\ \ S_4^{\,4} \equiv E$$

The S_2 operation does not exist, since it is equivalent to *i*

$$S_2 = \sigma_{xy} \times C_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = i$$

Optically active molecules: to be optically active a molecule must NOT possess any S_n symmetry axis.

B. Group Theory

Different molecules have different number and types of operations that leave them unchanged. Based on these differences, we can place molecules into groups.

A group is defined as a collection of operations possessing the following properties:

1. Closed under multiplication, such that the product of any two operations must result in an operation that is also in the group.
2. Every operation must have an inverse, such that for every operation there must be an operation that undoes the effect of the first operation (puts molecule back in starting point).

   The inverse of matrix A is A^{-1} (does not mean 1/A)

   $A \bullet A^{-1} = A^{-1} \bullet A = E$
3. Every group must have an identity operation, E.
4. All operations of the group are associative, such that

   $ABC = (AB)C = A(BC)$

   In other words, the multiplication of A and B first followed by multiplication by C should yield the same result as multiplying A by the product of B and C.

The symmetry operations of molecules form groups known as Point Groups (since there is always one point in the molecule that does not move when operations are performed).

Products of Operations

Before we continue the discussion of point groups, or groups in general, we need to know how to multiply symmetry operations.

The multiplication of A and B to yield C is given by

$$A \bullet B = C$$

If the operations are being performed on a molecule or point P, we can write

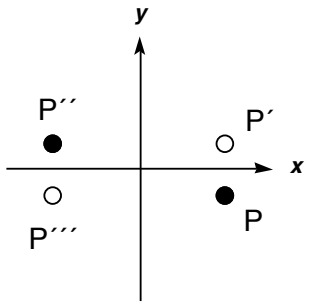
$$A \bullet B\,(P) = C\,(P),$$

where C is the result of performing operation B on point P first, and then doing operation A on the result. When operations are multipled, always perform the operations in the order from right to left.

The result of a product of operations can be determined *graphically* or *mathematically*. Both methods will be used to solve the example below. You can choose to use either method, just make sure that you know how to arrive at the correct answer.

Example: Consider the product of C_2^x and C_2^y, where C_2^x represents a C_2 rotation about the x-axis and C_2^y a C_2 rotation about the y-axis. Is there a single operation that equals the product? What is it? Do the operations commute?

First we will solve the problem graphically. To do this, draw the x- and y-axes on the plane of the paper and the z-axis coming out of page towards you. In addition, closed (filled) circles will denote a point positioned above xy-plane (positive z value) and open circles will be used for points below xy-plane (negative z values). Place a point, P, on the graph, placing closer to one axis than the other (this is an important point), as shown below.



We will write the multiplication of the operations as

$$C_2^y\ C_2^x\ (P) = C_2^y\ (P') = P''$$

where performing a C_2^x rotation on point P first results in point P´, followed by a C_2^y rotation on point P´ to yield the result, P´´. If the operations commute, then doing them in reverse order should give the same result. It can be shown graphically that performing C2y first on point P results in point P´´´. When C_2^x is performed on P´´´, the result is P´´.

$$C_2^x\ C_2^y\ (P) = C_2^x\ (P''') = P''$$

The question that remains is what single operation can take the point P to P´´. This operation is then the result of the multiplication of C_2^x and C_2^y. From inspection of the figure above, once can deduce that the operation C_2^z is the answer, such that

$$C_2^z\ (P) = P''$$

and, therefore,

$$C_2^y\ C_2^x = C_2^x\ C_2^y = C_2^z$$

To ensure that one indeed has arrived at the correct answer, it is good to repeat the exercise with a new point, P_1, starting at a different place in the graph. If C_2^z is indeed the result of the product, then $C_2^z (P_1) = P_1''$ and $C_2^z (P) = P''$.

The same solution for the multiplication can be obtained mathematically using the transformation properties of a Cartesian point P, where P = (a,b,c). We know that

$$C_2^z(a,b,c) = (-a,-b,c)$$

$$C_2^y(a,b,c) = (-a,b,-c)$$

$$C_2^x(a,b,c) = (a,-b,-c)$$

Therefore

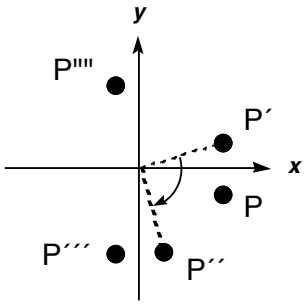
$$C_2^y C_2^x(a,b,c) = C_2^y(a,-b,-c) = (-a,-b,c)$$

or

$$C_2^y C_2^x(a,b,c) = C_2^z(a,b,c) = (-a,-b,c)$$

One can also multiply the transformation matrices for C_2^x and C_2^y. The resulting matrix will be the transformation matrix for C_2^z.

Example: What is the result of $C_4 \bullet \sigma_{xz}$? Do the operations commute?



$C_4 \bullet \sigma_{xz} (P) = C_4 (P') = P''$

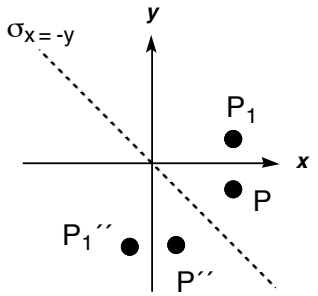
Do the operations commute? No, because

$\sigma_{xz} \bullet C_4 (P) = \sigma_{xz} (P''') = P''''$

From inspection, the single operation for $C_4 \bullet \sigma_{xz}$ that takes P to P'' is a reflection through a plane that contains the z-axis and the line x=-y, $\sigma_{x=-y}$, such that

$$C_4 \bullet \sigma_{xz} = \sigma_{x=-y}$$

In order to ensure this is correct, one can choose another point P_1, such as (4,2,3) as a test. Performing the multiplication graphically, $C_4 \bullet \sigma_{xz}$ (4,2,3) = (-2,-4,3). Again graphically as shown below, one can make sure that indeed $\sigma_{x=-y}$ (4,2,3) = (-2,-4,3) = P_1'' and that $\sigma_{x=-y} (P) = P''$.



In general,

$C_4 \bullet \sigma_{xz}\,(a, b, c) = C_4\,(a, -b, c) = (-b, -a, c)$

and

$\sigma_{x=-y}\,(a, b, c) = (-b, -a, c)$

Using the corresponding transformation matrices one can arrive at the answer mathematically as shown below.

$$C_4 \bullet \sigma_{xz} = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \sigma_{x=-y}$$

Use the resulting matrix as operation on a point (a, b, c) to arrive at the transformed point (-b, -a, c)

$$\begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix} = \begin{bmatrix} -b \\ -a \\ c \end{bmatrix}$$

Do the operations commute? No, since the resulting matrix is different, as shown below.

$$\sigma_{xz} \bullet C_4 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Usually, most multiplication problems can be solved graphically.

Constructing groups

If a molecule has a C_2^x axis and a C_2^y axis as symmetry elements (as operations), then both of these operations must belong to a group. But these two operations are unlikely to be the only two operations in the group. We can use the properties of groups defined earlier to arrive at all the other operations of a group.

To identify other elements in the group:

(1) The identify element, E, must be an operation of the group. All groups have E.

(2) Since closure under multiplication is a property of all groups, one can arrive at all the operations of the group by multiplying all elements known. The result of each multiplication must also be an element of the group.

The easiest way to arrive at all the operations of the group is to construct a group multiplication table. We start with the three elements we know on the top and left side, E, C_2^x, and C_2^y. The identity element, E, is always listed first on the table. Elements in the multiplication table are multiplied always in the same order, (column) x (row). All elements multiplied by E result in the element itself, therefore, the first column and first row yield the original elements as shown below.

	E	C_2^x	C_2^y
E	E	C_2^x	C_2^y
C_2^x	C_2^x		
C_2^y	C_2^y		

In addition, we know that $C_2^x \bullet C_2^x = E$ and $C_2^y \bullet C_2^y = E$, so we can add that result in the box where the corresponding column and row intersect. From the example earlier, we also know that $C_2^x \bullet C_2^y = C_2^y \bullet C_2^x = C_2^z$. This result is added in red in the table below.

	E	C_2^x	C_2^y
E	E	C_2^x	C_2^y
C_2^x	C_2^x	E	C_2^z
C_2^y	C_2^y	C_2^z	E

Since C_2^z is an operation that was not on the original multiplication table, it needs to be added to the top and left columns, as shown in blue below. This operation now needs to be multiplied with all the others in the group, shown in red, to ensure that it does not give rise to any additional operations. Since this is indeed the case, then the multiplication table below represents a complete group.

	E	C_2^x	C_2^y	C_2^z
E	E	C_2^x	C_2^y	C_2^z
C_2^x	C_2^x	E	C_2^z	C_2^y
C_2^y	C_2^y	C_2^z	E	C_2^x
C_2^z	C_2^z	C_2^y	C_2^x	E

Once one finishes completing the table, one should check that all the properties of a group are obeyed. For example, make sure that each element has an inverse. In this example, each element is its own

inverse, but this is not necessarily the case in other groups. By constructing the multiplication table, we have shown closure under multiplication, and we have included the identity element in the group.

The group in the multiplication table is one with elements

$$[\,E\,,C_2^{\,x}\,,C_2^{\,y}\,,C_2^{\,z}\,]$$

Each point group has a specific set of operations (or elements) associated with it, and each group has a name. As you will see in the next section, the point group with the elements above is **D_2**. Therefore, a molecule that belongs to the **D_2** point group will have E, $C_2^{\,x}$, $C_2^{\,y}$, and $C_2^{\,z}$ as operations that leave it unchanged. In such molecule, no other operations will be present. The common point groups and the operations associated with each point group will be discussed in the next section.

C. Symmetry Point Groups

Point symmetry: the symmetry of a molecule with respect to reflection, inversion, rotation, and improper rotation.

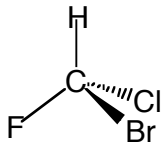
Point group: collection of symmetry operations that arise because of the existence of symmetry elements in a molecule.

Point Groups and Their Operations

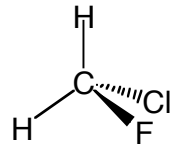
The common point groups and the operations associated with each group are listed below.

(1) Point groups with very low symmetry; no rotational axis in the molecule.

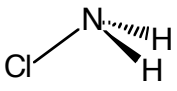
(a) **C_1**. If a molecule has only the identity operation, E, and no other operations present, then the molecule belongs to the point group **C_1**. An example is shown on the right.



(b) **C_s**. If the only operations in the molecules are a mirror plane and E, then its point group is **C_s**. Two examples are shown below.



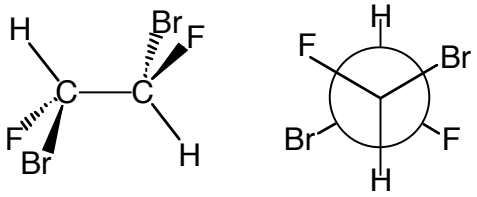
σ contains C,F,Cl



σ bisects H-N-H and contains N-Cl bond

(c) **C_i**. If the molecule only has the inversion operation, *i*, and E, then point group of the molecule is **C_i**. One example is 1,2-dibromo-1,2-difluoroethane in the staggered conformation shown below.

The Newman projection of the molecule is also shown for clarity. The center of inversion of the molecule is located at the center of the C-C bond.

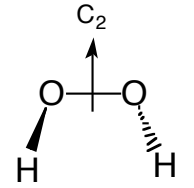


(2) Rotational Point Groups: $\mathbf{C_n}$, $\mathbf{C_{nh}}$, and $\mathbf{C_{nv}}$

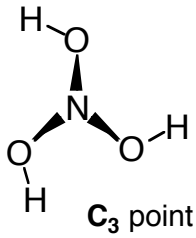
(a) $\mathbf{C_n}$. The only operations in the $\mathbf{C_n}$ point groups are C_n (and its repetition) and E.

The $\mathbf{C_n}$ point groups have a total of n operations: C_n, C_n^2, C_n^3, ... $C_n^n = E$

Examples of molecules that belong to the $\mathbf{C_2}$ and $\mathbf{C_3}$ point groups are shown below. Please note that there no other operations present in these molecules, such as mirror planes or inversion.



$\mathbf{C_2}$ point group



$\mathbf{C_3}$ point group

(b) $\mathbf{C_{nh}}$. This group has the operations of the Cn group with the addition of a horizontal mirror plane, σ_h, perpendicular to the C_n axis.

Operations of the $\mathbf{C_{nh}}$ point groups:

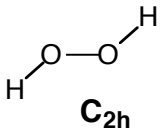
If n = even: C_n and its repetitions, σ_h, *i*, various S_n

If n = odd: E, C_n and its repetitions, σ_h, various S_n

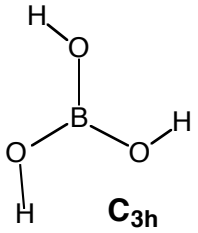
We always consider the C_n axis "vertical", and horizontal mirror planes are always perpendicular to the C_n axis (or the C_n axis of highest order).

Planar *trans*-HOOH is an example of a molecule that belongs to the $\mathbf{C_{2h}}$ point group. There is a C_2 axis perpendicular to the plane of the molecule and a mirror plane on the plane of the molecule. Additional operations present are *i* and E.

Similarly, planar $B(OH)_3$ belongs to the $\mathbf{C_{3h}}$ point group.



C_{2h}

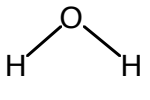


C_{3h}

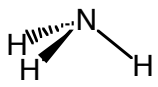
(c) **C_{nv}** : This group has the operations of the **C_n** group with the addition of vertical mirror planes, σ_v (these are mirror planes that contain the C_n axis).

- The mirror plane σ_v is reproduced n times in the **C_{nv}** point group
- The operations of the **C_{nv}** point group are: E, C_n and its repetitions, n σ_v
- **C_{nv}** point groups have a total of 2n operations

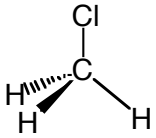
Some examples of molecules that belong to the **C_{nv}** point groups are shown below.



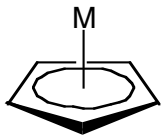
C_{2v}



C_{3v}



C_{3v}

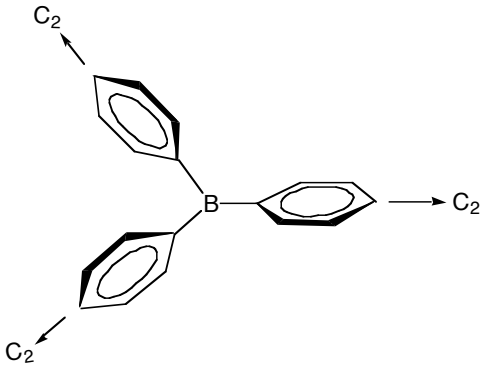


C_{5v}

(3) Dihedral point groups: **D_n**, **D_{nh}**, **D_{nd}**

(a) **D_n**: formed by the addition of a C_2 axis perpendicular to the C_n axis in the **C_n** point group
These point groups are not very common, since there are no mirror planes or inversion center.

- There are n C_2 axes perpendicular to the C_n axis
- There are a total of 2 n operations in the D_n point group

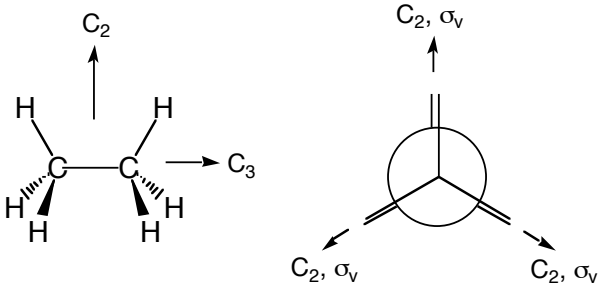


An example of a molecule that belongs to the **D_3** point group is shown on the left, with a trigonal planar central B atom and three phenyl rings at 45° from the of the plane of the central atom. A C_3 axis is present from the central B atom, perpendicular to the trigonal plane defined around the central atom. C_2 axes are present perpendicular to the C_3 axis.

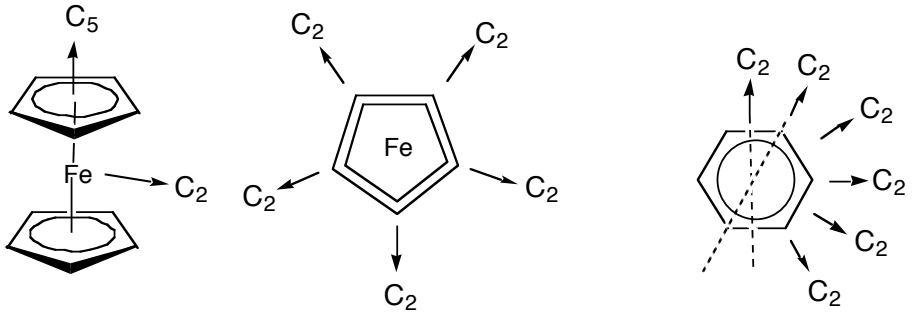
(b) **D_{nh}**: Formed by the addition of σ_h to the **D_n** point group (where $\sigma_h \perp C_n$ axis). This is a very common point group. The **D_{nh}** point groups also have n σ_v mirror planes that contain both the C_n and C_2 axes, where an n number of C_2 axes are present in the group).

Operations: C_n and its repetitions, n C_2's, σ_h, n σ_v's , *i* (if n is even), various S_n
Total number of operations = 4n

An example of a molecule that belongs to the **D_{3h}** point group is eclipsed ethane. As shown on the left, eclipsed ethane has a C_3 axis that contains the C-C bond and three C_2 axes perpendicular to C_3 with origin at the center of the molecule. A horizontal mirror plane, σ_h, is present, which contains all three C_2 axes and is perpendicular to the C_3 axis. In addition, vertical mirror planes, σ_v's, which contain both the C_3 axis and each C_2 axis are found.



Eclipsed ferrocene, shown below, is similar to eclipsed ethane. Eclipsed ferrocene belongs to the **D_{5h}** point group. Benzene, with a C_6 axis, 6 C_2 axes perpendicular to C_6, and a σ_h mirror plane, belongs to the **D_{6h}** point group.



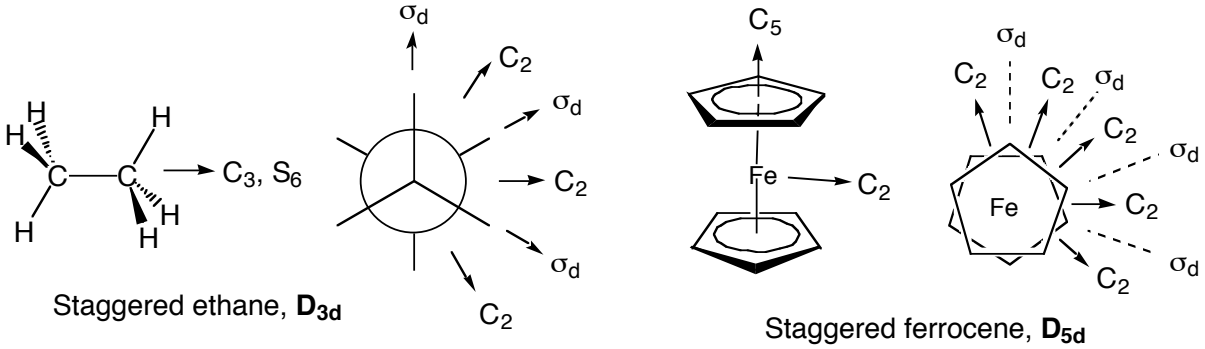
(c) **D_{nd}**: Formed by the addition of dihedral mirror planes, σ_v, to the D_n point group. There are n σ_v mirror planes that contain the C_n axis and bisect adjacent C_2 axes. This point group is quite common. The most identifiable difference between the **D_{nh}** and **D_{nd}** point groups is that **D_{nh}** has a σ_h mirror plane and **D_{nd}** does not.

Operations: C_n and its repetitions, n C_2's , n σ_d's, *i* (if n is odd), various S_n

An example of a molecule that belongs to the **D_{3d}** point group is staggered ethane. As shown below, staggered ethane has a C_3 axis that contains the C-C bond, however, it does not have a horizontal mirror plane perpendicular to the C_3 axis. The molecule has three C_2 axes that are perpendicular to C_3; these axes cross the center of the C-C bond. In addition, three dihedral mirror planes, σ_d, that contain C_3 but bisect adjacent C_2 axes are present. In

addition, the molecule has a center of inversion, *i*, and an S_6 axis overlapping with the C_3 axis.

In a manner similar to staggered ethane, staggered ferrocene belongs to the D5d point group. Some of the operations of staggered ferrocene are shown below.

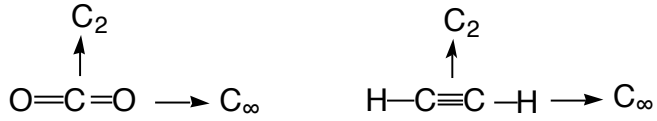


(4) Linear point groups: $\mathbf{C_{\infty v}}$, $\mathbf{D_{\infty h}}$

All linear molecules have a C_∞ axis that contains all the atoms in the molecules and an infinite number of σ_v planes that contain the C_∞ axis

$C_{\infty v}$: no C_2 axis $\perp$ to C_∞ or σ_h mirror plane ($\perp$ to C_∞)
Operations: C_∞, ∞ σ_v's

$D_{\infty h}$: C_2 axis $\perp$ to C_∞ and σ_h mirror plane $\perp$ to C_∞
Operations: C_∞, ∞ σ_v's, σ_h, ∞ C_2's, *i*

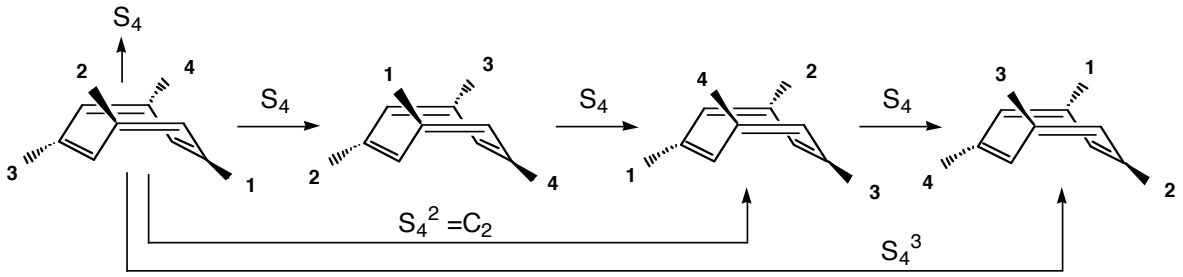


(5) The **S_n** groups. These point groups are very uncommon, since they only have the S_n operation and its repetitions.

Operations: S_n, S_n^2, ... $S_n^n = E$

There are a total of n operations in an **S_n** point group.

Example: 1,3,5,7-tetramethylcytoclooctatetraene



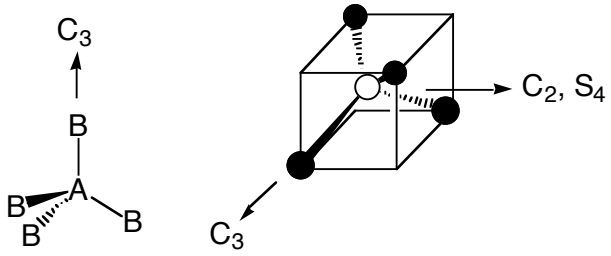
In this example, the methyl groups are numbered to show the effect of sequential rotations about the S_4 axis. An important point is that the C_2 axis in the molecule derives from the presence of S_4^2. This molecule belongs to the **S_4** point group, with operations S_4, $S_4^2 = C_2$, S_4^3, and E.

(6) Very high symmetry point groups: **T_d**, **O_h**, **I_h**

These groups are characterized by more than one axis of n ≥ 3 and are contain of the cubic and icosahedarl groups. In these groups all vertices, edges, and faces are equivalent.

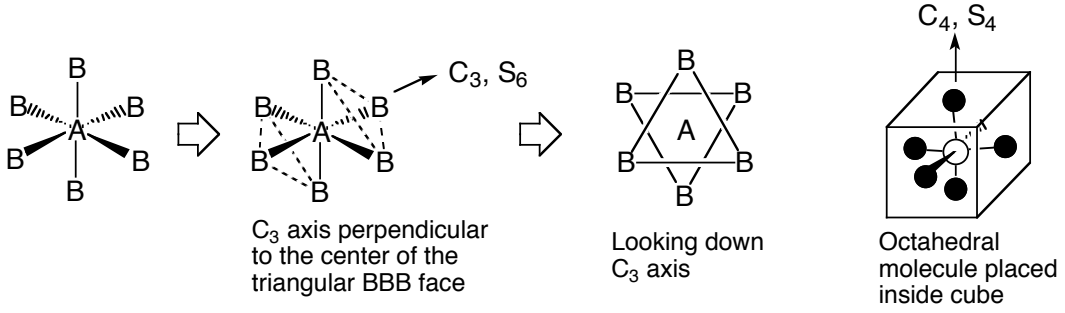
(a) Tetrahedral point group: **T_d**. Example: CH_4

C_3, C_3^2 down each A—B: 8 operations



C_2 bisecting B—A—B:	3 operations
S_4, S_4^3 along same:	6 operations
σ_d's through opposite edges:	6 operations
E:	1 operation
TOTAL:	24 operations

(b) Octahedral point group: **O_h**. Example: PF_6^-

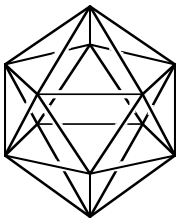


Operations:

C_3, C_3^2 through each BBB face (through corners of cube):	8 operations
C_2 bisecting B—A—B (through opposite edges of cube):	6 operations
C_4, $C_4^2 \equiv C_2$, C_4^3 down each BAB bond (through faces of cube):	9 operations
plus *i*, 6 S_4, 8 S_6, 3σ_h, 6 σ_d, and E	25 operations
TOTAL:	48 operations

(c) Icosahedral point group: $\mathbf{I_h}$ (120 operations total)

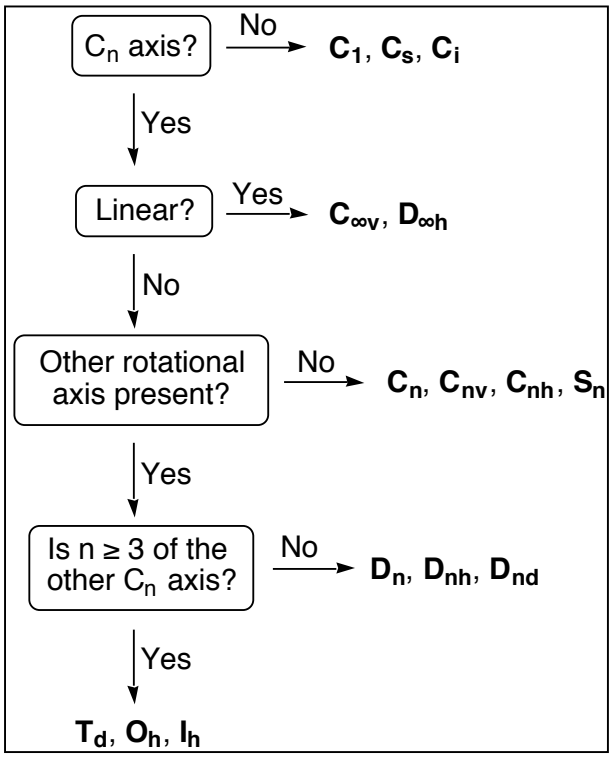
Icosahedron: 12 vertices, faces: 20 equilateral triangles ($B_{12}H_{12}^{2-}$)



Dodecahedron: 20 vertices, faces 12 regular pentagons

Determination of Point Groups

In the discussion of point groups above, all groups were listed and examples were provided. However, usually the situation is in reverse, such that one is given a molecule and one needs to assign a point group to it. So, how does one determine the point group of a molecule? One can follow the simplified flowchart on the right. A more complete chart can be found in your book. In general, it is first important to determine whether the molecule has a rotational axis, C_n. If it does not, then it must belong to one of the very low symmetry point groups, $\mathbf{C_1}$, $\mathbf{C_s}$, or $\mathbf{C_i}$. If does possess a C_n rotational axis, one must determine if molecule is linear; if so, then its symmetry point group must be either $\mathbf{C_{\infty v}}$ or $\mathbf{D_{\infty h}}$. If the molecule is not linear and does not possess any rotational axes other than C_n, then it must belong to one of the rotational point groups, $\mathbf{C_n}$, $\mathbf{C_{nv}}$, $\mathbf{C_{nh}}$, or $\mathbf{S_n}$. However, if the molecules has C_2 axes perpendicular to Cn, then its symmetry point group is dihedral, either $\mathbf{D_n}$, $\mathbf{D_{nh}}$, or $\mathbf{D_{nd}}$. If rotational axes, C_n, with $n \geq 3$ are present in addition to the original C_n axis, then the molecule belongs to one of the very high symmetry point groups, $\mathbf{T_d}$, $\mathbf{O_h}$, or $\mathbf{I_h}$. Within each class of groups, other operations present, such as mirror planes, determine which particular point group the molecule belongs to. For example, in the rotational groups, $\mathbf{C_n}$, $\mathbf{C_{nv}}$, and $\mathbf{C_{nh}}$, the presence of a C_n axis and a σ_h mirror plane (in the absence of any other rotational axes) places the molecule in the $\mathbf{C_{nh}}$ point group. Similarly, the presence of a C_n and σ_v's (only) makes the molecule of $\mathbf{C_{nv}}$ symmetry.



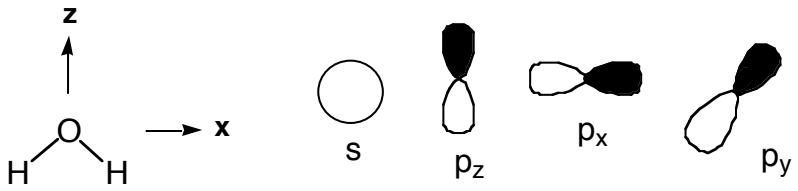
D. Introduction to Representations

The symmetry of molecules is important in bonding, since only orbitals of the same symmetry are able to interact (or mix) to form bonds. Therefore, in order to know if two orbitals can combine to form a bond, one needs to be able to determine the symmetry of orbitals within molecules. Keep in mind that each molecule belongs to a point group and that the point group has a certain set of operations associatedwith it. In order to determine the symmetry of an orbital, one must follow what happens to each orbital in question when the operations of the group are performed on it.

For example, consider a H_2O molecule, which belong to the $\mathbf{C_{2v}}$ point group. In the $\mathbf{C_{2v}}$ point group, the operations present are:

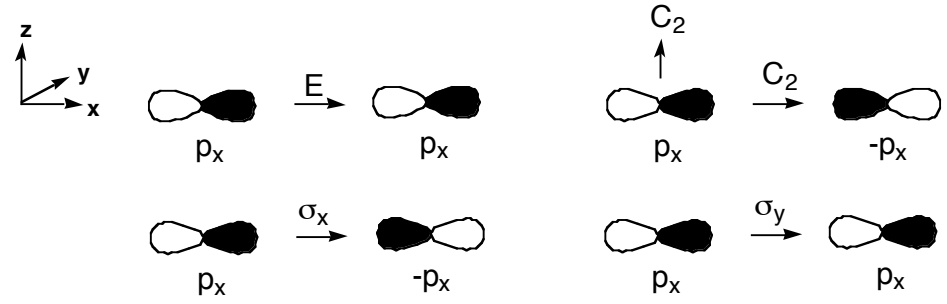
$$\mathbf{C_{2v}}\text{: } \{E, C_2, \sigma_x, \sigma_y\}$$

Recall that $\sigma_x = \sigma_{yz}$ and $\sigma_y = \sigma_{xz}$, mirror planes containing the yz-plane and xz-plane, respectively. Consider then the valence orbitals on the oxygen atom, the 2s and 2p orbitals using the coordinate system defined below.



Recall the orbitals are mathematical functions and that the shaded are non-shaded portions of the orbitals represent positive and negative parts of the function. In order to assing symmetry to orbitals, the question that must be asked is what happens to each of these orbitals as we perform the operations of the group (the point group of the molecule). In order to do this, we construct a table with the operations of the group along the top as shown below. Starting with the p_x orbital, we write "p_x" on the left side of the first row of the table. As shown below, performing each operation of the C_{2v} point group on p_x results either in the same function (unchanged, p_x) or the negative of the function ($-p_x$). These are entered on the table below.

	E	C_2^z	σ_x (σ_{yz})	σ_y(σ_{xz})
p_x	p_x	$-p_x$	$-p_x$	p_x



Similarly, the procedure is repeated for the p_y, p_z, and s orbitals and the results are entered on the table as shown below.

	E	C_2^z	σ_x (σ_{yz})	σ_y(σ_{xz})
p_x	p_x	- p_x	- p_x	p_x
p_y	p_y	- p_y	p_y	- p_y
p_z	p_z	p_z	p_z	p_z
s	s	s	s	s

Since the resulting functions are either themselves or their negative, we simply use the coefficients, as shown in the table below.

	E	C_2^z	σ_x (σ_{yz})	σ_y(σ_{xz})
p_x	1	- 1	- 1	1
p_y	1	- 1	1	- 1
p_z	1	1	1	1
s	1	1	1	1

These coefficients represent the trasnformation properties for a given orbital within a particular point group. Because the p_z and s orbitals have all the same coefficients, they transform the same under the operations of the $\mathbf{C_{2v}}$ point group. The transformation properties (set of coefficients) define a representation.

Therefore, in the example above,

p_x and p_y belong to two different representations

p_z and s belong to a third representation

A fundamental rule of representations is that two functions, operators, etc. cannot interact (mix) if they belong to different representations. Such interactions are symmetry forbidden. Mixing can only occur if two (or more) functions, operators, etc. belong to the same representation or if there is another element the helps mixing. The latter point will be discussed in more detail a later time.

Representations have labels. These labels are used to indicate the symmetry of different representations, therefore, if representations with different coefficients must have different labels. Here some of the most common labels will be summarized. Please keep in mind that as the point groups become more symmetric, additional subscripts are necessary to differentiate among representations. This labeling is beyond the scope of the present discussion.

The major label of a representation is a capital letter. This letter is associated with the number under the identity operation in the representation.

A or B: These labels are used for singly degenerate representations, where there is a 1 under the identity operation, E. This means that only one object is transformed. Which label is used is determined by whether the C_n operation yields a +1 or –1 as follows.

A if C_n operation yields +1

B if C_n operations yields –1

E: This label is used to denote doubly degenerate representations, where two equivalent objects must be transformed together, resulting in a 2 under the identity operation. An example is the x and y axis is $\mathbf{D_{4h}}$ symmetry. An example will be shown below.

T: This letter is used to denote triply degenerate representations, where three equivalent objects are transformed together. This results in a 3 under the E operation. An example are the three p orbitals, p_x, p_y, and p_z, in the $\mathbf{O_h}$ point group.

In addition to the capital letters, usually subscripts are necessary to further differentiate among representations. Only the subscripts "1" and "2" and "g" and "u" will be discussed here. Additional subcripts or labels are beyond the scope of this discussion.

Subscripts "1" and "2" are used as follows:

1 is used if ($C_2 \perp C_n$) or $\sigma_v \perp$ to plane of molecule yield +1

2 is used if ($C_2 \perp C_n$) or $\sigma_v \perp$ to plane of molecule yield –1

Subscripts "g" and "u" are always used if there is a center of inversion in addition to any other subscripts

g is used if the object is symmetric with respect to inversion (*i* yields +1)

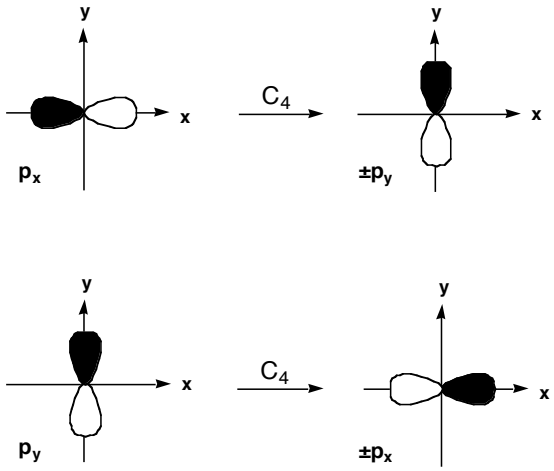
u is used if the object is not symmetric with respect to inversion (*i* yields –1)

In the H_2O example all the representations are singly degenerate, therefore, all letter labels must be either "A" or "B". In this example, there is no C_2 axis perpendicular to the main C_n axis, which in this case is C_2. Therefore, the mirror plane perpendicular to the plane of the molecule, σ_x, is used to determine whether a representation will hava an "A" or "B" label. The representations for the p_z and s orbitals, with a +1 under the σ_x operation, are both of "A" symmetry, whereas the symmetries of the p_x and p_y orbitals are "B". However, additional subscripts are necessary in order to differentiate among the representations for p_x and p_y, since both of them are "B". The labels are shown in the table below.

	E	C_2^z	σ_x (σ_{yz})	σ_y(σ_{xz})	Label
p_x	1	- 1	- 1	1	B_2
p_y	1	- 1	1	- 1	B_1
p_z	1	1	1	1	A_1
s	1	1	1	1	A_1

In the example above we can say that the p_x orbital has B_2 symmetry and that is a b_2 orbital. Similarly, the p_y orbital has B_1 symmetry and is a b_1 orbital. Both the p_z and s orbitals have A_1 symmetry and are a_1 orbitals. It is important to note that orbitals are written in lower cases, whereas the symmetry is expressed in upper case.

As mentioned above, some orbitals (or functions) transform together in certain point groups. The p_x and p_y orbitals in the **D_{4h}** point group will be used as an example of orbitals that transform together. The p_x and p_y orbitals are drawn on the right, showing that a C_4 rotation, an operation of the **D_{4h}** point group, exchanges the functions. This means that a C_4 rotation on p_x results in $\pm p_y$, and C_4 on p_y results on $\pm p_x$. Therefore, unlike the example with the H_2O molecule above, there is at least one operation in the group that exchanges the two orbital functions. This is the reason why the two cannot be separated and must be treated together. When this happens, a "2" must be entered under the identity operation.



The table with the operations of the **D_{4h}** point group is shown below. In the first row, the p_x and p_y orbitals are treated together. Whenever an operation exchanges or mixes two functions, a "0" is entered under that operation. For all other operations, the sum of what happens to each orbital is added. For example, the C_2^z operation on p_x results on $-p_x$, or -1. Since the C_2^z operation on p_y also results on -1, then the sum of the two is -2, which is entered in the table. The same results is obtained for *i*.

D_{4h}	E	$2C_4^z$	C_2^z	$2C_2'$	$2C_2''$	*i*	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_v'$	
p_x and p_y	2	0	-2	0	0	-2	0	2	0	0	E_u
d_{xy}	1	-1	1	-1	1	1	-1	1	-1	1	B_{2g}
d_{yx} and d_{xz}	2	0	-2	0	0	+2	0	-2	0	0	E_g

The σ_h operation results in +1 for both p_x and p_y, for a total of 2. The S_4, C_2'', and σ_v' operations exchange the functions of px and py, thus resulting in a zero. The C_2' operation along one of the axis, for example the x-axis, will result in a +1 for p_x and a –1 for p_y, therefore the sum is a zero. The same occurs for the σ_v operation. Because there is a "2" under E and under inversion there is a negative number, the symmetry label (on the far right of the table) is E_u.

The d_{xy} orbital can be treated alone in the **D_{4h}** point group, since none of the operations of the group exchange its function with any other orbtital. Therefore, a "1" is placed under E and all operations of the group result in either +1 or –1. The –1 under C_4 results in a B symmetry label, and the –1 under C_2' results in the subscript "2". Since there is a +1 under *i*, then the symmetry label for this representation is B_{2g}.

As in the case of the p_x and p_y orbitals, the d_{xz} and d_{yz} orbitals transform together in the **D_{4h}** point group as shown in the table. The result is a representation with E_g symmetry.